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(54) Title: PROCEDURE FOR BLEACHING CELLULOSE PULP

(57) Abstract

The present invention concerns a procedure for bleaching cellulose pulp obtained from hardwood, wherein bleaching chemical containing chlorine is used. The essential feature of the invention is that the residual chlorine content of the bleached pulp is reduced by subjecting the pulp to enzyme treatment. With the enzyme especially the removal from the pulp of chlorine-binding extractive substances present in hardwood pulp is promoted. The invention furthermore concerns the use of enzyme towards lowering the residual chlorine content of bleached cellulose pulp made from hardwood. Such cellulose pulp is particularly contemplated which will be converted into foodstuff package cardboard or paper, which are commonly disposed of by burning. Lowered chlorine content reduces the risk of producing toxic dioxin at the incineration step.

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PROCEDURE FOR BLEACHING CELLULOSE PULP

The present invention concerns a procedure for bleaching cellulose pulp derived from hardwood, a bleaching chemical containing chlorine being used in said procedure.

Cellulose pulp obtained by sulphate cooking in particular is brown, mainly owing to lignin remaining in the pulp. The present understanding is that this residual lignin is linked to hemicellulose with covalent bonds. Lignin is removed by bleaching, whereby the pulp is rendered usable for high-quality paper and cardboard products.

Bleaching is usually accomplished in a multi-stage process in which the pulp is alternately treated with oxidizing, lignin-decomposing chemicals and with chemicals dissolving the substances generated as decomposition products. Above all, substances containing chlorine have been used for oxidizing chemicals, such as pure chlorine gas, chlorine dioxide or sodium or potassium hypochlorite, although other types of oxidizing bleaching agents containing no chlorine are also known. For extraction chemicals removing the decomposition products, alkali solutions have been used.

In the course of reacting, chemicals containing chlorine cause chlorination of lignin, as well as of such fatty and resinous acids which are present in the pulp. Therefore chlorophenols are produced from lignin in the bleaching process, which end up in the bleaching waste water escaping from the pulp. Chlorine is further bound to those residues of lignin and acids which are still left in the cellulose pulp after completed bleaching. In recent time this residual chlorine has been increasingly regarded as an environmental detri-

ment at the phase when paper or cardboard products made from the pulp end up as waste, and restriction imposed on the allowable chlorine content of pulp are therefore to be expected on the near future. Such restrictions would particularly concern pulp used for foodstuff cardboard which ends up in waste incineration plants and on dumps. This problem is particularly salient in the case of pulp made from hardwood, e.g. from birch or eucalyptus wood, which has a high content of chlorine-binding extractive substances.

The object of the present invention is therefore to devise a problem solution by which the residual chlorine content of bleached cellulose pulp made of hardwood can be reduced from the present level. The invention is characterized in that the residual chlorine content is lowered by subjecting the pulp to an enzyme treatment.

It has already been observed in earlier studies that it is possible with the aid of enzymes to detach lignin from cellulose. The conclusion herefrom is that when pulp obtained in a cooking process is first treated with enzyme, the use of chlorine-containing bleaching chemicals in the subsequent bleaching step can be eliminated, partly or even totally. In the present invention now the observation has been made that when said enzyme treatment is combined with a bleaching process using chlorine chemicals in substantially standard manner, the result will be cellulose pulp having a residual chlorine content which is substantially lowered from what it would be in the absence of enzyme treatment.

According to the invention, the enzyme treatment may be carried out at an arbitrary stage of the bleaching process. Thus, the pulp may be treated with enzyme in connection with one of the oxidizing steps or extraction

steps (alkali steps) of the process or between the respective steps, prior to said bleaching steps, or not until after said steps. The enzyme to be used is advantageously hemicellulase, cellulase, esterase or a mixture of these, and as suitable enzyme products may be mentioned Multifekt L 250 and Multifekt K. The temperature of the enzyme treatment may be in the range of 10 to 90°C, preferably 40 to 70°C, and pH within the range of 3.0 to 7.5, preferably 4.0 to 6.0.

A further object of the invention is the use of enzyme towards reducing the residual chlorine content of bleached cellulose pulp made from hardwood. Suitable enzymes include hemicellulases, cellulases and esterases or mixtures of these, e.g. the enzyme products Multifect L 250 and Multifect K. Use of the enzyme is implemented, according to the invention, in the manner set forth in the preceding description of the bleaching procedure.

Quite specifically the use of enzyme as taught by the invention relates to reduction of the residual chlorine content in bleached cellulose pulp meant to be processed into foodstuff packaging cardboard or paper. This is because the increasingly stricter provisions regarding residual chlorine concern particularly said cardboard and paper brands, which end up as waste for disposal in waste incineration plants, where the chlorine contained in them may, when it burns, produce highly toxic dioxin.

The appropriate enzyme activities (U = unit of activity) of various enzyme categories that can be used in the present invention are within the following limits:

Hemicellulases:	
e.g. xylanase	0 to 10^6 U per kg of mass [1]
β-xylosidase	0 to 20,000 U per kg of mass [2]
Esterases:	0 to 100,000 U per kg of mass
Cellulases:	
Filter paper activity	0 to 20,000 U per kg of mass [3]
CMC activity	0 to 500,000 U per kg of mass [4]
β-glucosidase	0 to 20,000 U per kg of mass [5]
β-glucanase	0 to 500,000 U per kg of mass [4]

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The invention is described more closely in the following with the aid of two embodiment examples based on laboratory experiments.

Example 1

220 g pulp dry matter from birch sulphate cooking (dry weight content of pulp 10%) were suspended into 50 mM

of Na nitrate buffer pH 5 in such manner that the ultimate concentration of the mixture was 2.5%. Multifect K enzyme was added so that the xylanase activity of the mixture was 56 U per g of pulp dry matter. The temperature during the enzyme treatment was 39°C and treatment time, 20 h. The pulp was filtered after enzyme treatment with a Büchner funnel and the pulp cake thus obtained was washed with ion-exchanged water so as to obtain a washing ratio of 28.

A similar pulp batch was treated as reference in the same manner but without enzyme addition.

In Table Ia below are presented results of measurement from said two pulp stock batches, in this step of treatment.

TABLE Ia

	Enzyme treated	No enzyme treatment (Reference batch)
Kappa number	16.8	21
DKM extract content (% of dry matter)	0.27	0.23
Consistency (dm³/kg)	1065	1280

The enzyme-treated pulp stock batch and the reference batch were next subjected to bleaching, which took place in five consecutive oxidizing and extracting steps. In the first step chlorine and chlorine dioxide were used for chemicals, in the second step sodium hydroxide, in the third step chlorine dioxide, in the

fourth step sodium hydroxide, and in the fifth step chlorine dioxide. In The following Table Ib are presented the total chlorine quantities used in bleaching, and the results of measurement found with the bleached pulp batches.

TABLE Ib

	Enzyme treated	No enzyme treatment (Reference batch)
Dosage of active chlorine, (mg/g of pulp dry matter) (2 x kappa)	33.6	42
Yield	93.6%	97.5%
DKM extract content, % of dry matter	0.26	0.29
Consistency (dm^3/kg)	1035	1210
Residual chlorine content (mg/g)	0.845	1.270

The results reveal that the residual chlorine content after bleaching is clearly lower in the enzyme-treated cellulose pulp than in the pulp which received no enzyme treatment. It is further seen that no decisive weakening of strength values took place in the enzyme-treated pulp.

Example 2

In this experiment three pulp stock batches obtained by birch sulphate cooking were used, which had the same consistency as those in the preceding Example 1. Two batches were treated with enzyme as presented above, while the third batch constituted a reference batch. The enzymes differed from those used in Example 1 in that with one of them (in Batch 1) in the mixture was achieved, in addition to xylanase activity 56 U per g of pulp dry matter, cellulase activity 1.5 U per g of pulp dry matter and in the other (Batch 2), in addition to xylanase activity 56 U per g of pulp dry matter, cellulase activity 1.1 U per g of pulp dry matter. The results after enzyme treatment are shown in Table IIa.

TABLE IIa

	Enzyme pre-treatment (Batch 1)	Enzyme pre-treatment (Batch 2)	No enzyme treatment (Reference batch)
Kappa number	15.8	15.0	18.8
DKM extract content (% of dry matter)	0.32	0,32	0.26
Consistency (dm^3/kg)	1025	1130	1305

The pulp batches were hereafter bleached with chlorine chemicals and sodium hydroxide as in Example 1. The total chlorine dosage in mg/g was 2 x the kappa number in each case. The results after bleaching are shown in Table IIb.

TABLE IIb

	Enzyme pre-treatment (Batch 1)	Enzyme pre-treatment (Batch 2)	No enzyme treatment (Reference batch)
Yield	94.6	-	97,4
DKM extract content (% of dry matter)	0.36	0,35	0.37
Consistency (dm^3/kg)	980	1065	1210
Total chlorine content (mg/g)	1.15	1.15	1.46

The results reveal in this instance, too, that enzyme treatment substantially reduces the residual chlorine content of the bleached pulp.

Example 3

Bleached birch sulphate pulp was used in this experiment. The pulp had been bleached using for bleaching chemicals in the first step chlorine (90%) and chlorine dioxide (10%), in the second step sodium hydroxide and in the third step oxygen.

The bleached pulp was subjected to enzyme treatment under identical conditions, and using the same enzyme, as in Example 1. After treatment, the pulp was washed with water and dried at room temperature. The residual chlorine content was measured both of the enzyme-treat-

ed pulp and of the untreated, original bleached sulphate pulp, the result 1.18 being found for the former and 1.56 mg/g for the latter. Thus, the residual chlorine content of bleached pulp could be substantially lowered by means of enzyme treatment.

The test demonstrates that the desired result is attained with the invention also in case the cellulose pulp is first bleached and treated with enzyme only thereafter.

It is obvious to a person skilled in the art that different embodiments of the invention are not confined to what has been presented in the foregoing by way of example, and that they may vary within the scope of the claims following below. For instance, one may in the first step of conventional five-step chlorine bleaching use either chlorine alone or chlorine in mixture with chlorine dioxide. It is also possible to make the time during which the enzyme is allowed to act considerably less than the mentioned time of 20 hours. Treatment tomes of a few hours, or even shorter than one hour, are thus conceivable, depending on the enzyme chosen and on its activity.

CLAIMS

1. A procedure for bleaching cellulose pulp obtained from hardwood, wherein bleaching chemicalk containing chlorine is used, characterized in that the residual chlorine content of the bleached pulp is reduced by subjecting the pulp to enzyme treatment.

2. Procedure according to claim 1, characterized in that the pulp is treated with enzyme either before or after the bleaching treatment.

3. Procedure according to claim 1, characterized in that the enzyme treatment takes place within the temperature range 10 to 90°C, preferably 40 to 70°C, and at pH 3.0 to 7.5, preferably 4.0 to 6.0.

4. Procedure according to any one of the preceding claims, characterized in that the enzyme which is used is hemicellulase, cellulase, esterase or a mixture of these.

5. Procedure according to claims 2-4, characterized in that to unbleached pulp obtained by birch sulphate cooking is added enzyme which is allowed to act, whereafter the pulp is subjected to bleaching comprising consecutive oxidizing and extracting steps, using for bleaching chemicals in the oxidizing steps chlorine gas and/or chlorine dioxide and in the extracting steps, sodium hydroxide.

6. Procedure according to claim 5, characterized in that the bleaching is a five-step chlorine bleaching.

7. Procedure according to claims 2-4, characterized in that pulp obtained by birch sulphate cooking is bleached in consecutive oxidizing and extracting steps, using

in the first step chlorine gas and/or chlorine dioxide and in the subsequent extracting step, sodium hydroxide, and that after bleaching to the pulp suspension thus obtained is added enzyme, which is allowed to act the desired time.

8. The use of enzyme for lowering the residual chlorine content of bleached cellulose pulp made from hardwood.

9. The use according to claim 8 of hemicellulase, cellulase, esterase or a mixture of these towards lowering the residual chlorine content of bleached cellulose pulp.

10. The use of enzyme according to claim 8 or 9 towards lowering the residual chlorine content of bleached cellulose pulp that is going to be processed to become foodstuff package cardboard or paper.

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI89/00045

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC 4

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II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC 4	D 21 C
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Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched [8]

SE, NO, DK, FI classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	Viikari, L. et al, "Bleaching with enzymes", Biotechnology in the Pulp and Paper Industry, The third International Conference, Stockholm June, 16-19, 1986, p 67-69	1-6, 8-10
X	Viikari, L. et al, Nordisk Cellulosa, Vol. 5, 1988, No. 2, p 63, 65, 66	1-6, 8-10

* Special categories of cited documents: [10]

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IV. CERTIFICATION

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